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U.S. Department  
of Transportation

United States  
Coast Guard



Commandant  
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JUN - 3 1993

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Dockets Unit (Docket HM-214)  
Research and Special Programs Administration  
Department of Transportation, Room 8421  
400 Seventh Street, SW  
Washington, DC 20590-0001

Dear Sir or Madam:

During recent public hearings on the Oil Spill Prevention and Response Plan Interim Final Rule (Docket HM-214), it was apparent that many speakers and attendees were not familiar with the definition of oil provided in section 311 of the Federal Water Pollution Control Act (FWPCA)(33 U.S.C. 1321, et seq). The Coast Guard is particularly concerned that the definition of oil, as provided in the FWPCA, remain as stated in statute and regulation.

Since 1970, the FWPCA has defined oil as follows: "oil means oil of any kind or in any form, including, but not limited to, petroleum, fuel oil, sludge, oil refuse, and oil mixed with wastes other than dredged spoil" (33 U.S.C. 1321(a)(1)). This same definition is used in the Coast Guard's regulations on facilities transferring oil or hazardous materials in bulk (33 CFR Part 154). Under this broad definition, the Coast Guard includes coconut oil, shale oil, olive oil, mineral oil, linseed oil, peanut oil, fats, greases, and petroleum derived oil. While the Coast Guard has not developed an exhaustive list of substances that are considered oil, it has broadly interpreted the definition of oil.

The Oil Pollution Act of 1990 (OPA 90) did not amend the definition of oil contained in subsection 311(a) of the FWPCA. Section 4202 of OPA 90 amends subsection 311(j) of the FWPCA by adding, among other paragraphs, a new paragraph requiring tank vessel and facility response plans. Therefore, the requirements for response plans for tank vessels and facilities are dependent on the definition of oil as taken from the unchanged definition contained in subsection 311(a) of the FWPCA. Under this definition, non-petroleum oils, such as agricultural oils and edible oils, are and have always been considered oils.

The Coast Guard's marine environmental response and pollution prevention programs are tied to the definition of oil provided in section 311(a) of the FWPCA. Consistent with this, the Coast Guard requires that response plans and operations manuals be prepared and submitted to the Coast Guard under section 311(j) of the FWPCA for marine transportation-related facilities that handle, store, or transport petroleum or non-petroleum oils. The Coast Guard

Subj: COAST GUARD COMMENTS TO RSPA DOCKET HM-214

routinely prepares reports of violation of section 311(b)(3) of the FWPCA for discharges onto navigable waters of petroleum and non-petroleum oils in quantities which may be harmful. When all elements of a violation are present, a civil penalty is assessed against the responsible party. Similarly, the Environmental Protection Agency also applies the same definition of oil in its Spill Prevention Control and Countermeasure Program (SPCC) (40 CFR Part 112). Therefore, any non-transportation-related facility that handles or stores petroleum oil or non-petroleum oil is subject to the EPA SPCC program, and may be required to prepare and submit facility response plans when it is determined that they could reasonably be expected to cause substantial harm to the environment.

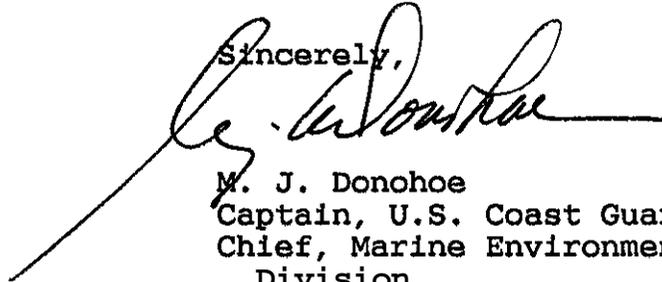
Several speakers at the recent public hearing on Docket HM-214 commented that Congress did not intend to use such a broad definition of oil and that response plans were intended only for petroleum oils. This is incorrect. The FWPCA definition of "oil" was not modified by OPA 90. On page 102 of the Conference Report on OPA 90, the definition of the term "oil" in OPA 90 is based on the definition of oil in section 311 of the FWPCA. The slight modification in the OPA 90 definition of oil is clearly attributed in the Conference Report to clarifying that oil does not include any hazardous substance covered by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA). This modification ensures that there will be no overlap in the liability provisions of CERCLA and OPA 90. It also ensures use of the appropriate Federal funds for removal of oil and CERCLA hazardous substances. An earlier draft of the Oil Pollution Act contained a much narrower definition of oil limiting the term to petroleum oil. The House Committee on Merchant Marine and Fisheries noted that the narrower definition of oil would not include non-petroleum oil or products such as whale or vegetable oil. Based on the broader language finally adopted in Title I of OPA 90, it is clear that Congress intended only to clarify the definition of oil, as contained in Title I of OPA 90.

The environmental effects of discharges of non-petroleum oils are clearly documented and are, in many respects, similar to the environmental effects of discharges of petroleum oils. These effects are attributed to similarity in physical properties of both petroleum and non-petroleum oils. During the public hearing, Ms. Jan Thurman with the Department of Interior discussed these impacts very briefly. She expressed her intent to provide detailed information to the docket on the environmental impact of non-petroleum oils when discharged to navigable waters. I have enclosed information on the impact of various non-petroleum oils from the National Oceanic and Atmospheric Administration Biological Assessment Team. I am also providing several articles on the properties and effects of non-petroleum oils.

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Thank you for the opportunity to provide this information to Docket HM-214.

Sincerely,



M. J. Donohoe  
Captain, U.S. Coast Guard  
Chief, Marine Environmental Protection  
Division

By direction of the Commandant

- Encl:
- (1) Information on selected non-petroleum oils from NOAA Biological Assessment Team
  - (2) "Birds Affected by a Canola Oil Spill in Vancouver Harbour, February, 1989," Spill Technology Newsletter, October-December, 1989
  - (3) "Canola Oil as a Substitute for Crude Oil in Cold Water Tests," Spill Technology Newsletter, January-February, 1983
  - (4) "Properties and Effects of Non-Petroleum Oils," Hans J. Crump-Weiner and Allen L. Jennings, from the 1975 Conference on Prevention and Control of Oil Pollution

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U.S. DEPARTMENT OF COMMERCE  
National Oceanic and Atmospheric Administration  
NATIONAL OCEAN SERVICE  
OFFICE OF OCEAN RESOURCES CONSERVATION AND  
ASSESSMENT  
Hazardous Materials Response and Assessment Division  
c/o USCG Commandant (G-MEP)  
2100 Second St., S.W., Room 2100  
Washington, D.C. 20593

June 3, 1993

MEMORANDUM FOR: THE RECORD

FROM: NOAA Hazardous Materials Response and Assessment  
Division

SUBJECT: Non-Petroleum Oils

Non-petroleum oils have a range of effects on the environment when spilled, depending on their properties. The following is a listing of their physical/ chemical properties, and toxicities.

Edible oils: coconut, corn, cottonseed, fish, palm - Physical/Chemical Properties

Coconut and palm oil can solidify at room temperatures and coconut oil is almost insoluble in water, therefore these oils will float on water and would be unlikely to form emulsions (Merck 1989; USCG 1985). Coconut and palm oils are very viscous and are used as emulsifying agents. When spilled in most coastal waters, they would behave like Crisco and probably persist for over a decade.

Corn oil would behave similarly to coconut oil, except that it would not emulsify as readily. A Canadian paper suggested using Canola oil (probably similar to corn and cottonseed oils) as a substitute for crude oil in cold water spill tests, suggesting that properties and behavior would be similar for these two oil. Emulsification tests using Canola oil showed that it resisted emulsification, but took on approximately 10% of the original water volume as a stable portion of the overlying oil. This behavior was very similar to the crude oil tested (Allen 1983).

Cottonseed oil has a density and viscosity of a slightly weathered medium crude, but evaporates slower than crude oil. It does not emulsify to any great extent. It would likely disperse completely within 3-5 days, particularly if the waters into which it was spilled were highly turbulent.

Fish oil has a density and viscosity of heavy crude, but would likely not emulsify readily and has a higher interfacial tension with water. These oils tend to dissipate rapidly, probably through dispersion in the water column or biodegradation, however evaporation is very slow. It is likely that the oil would completely disperse in three days, particularly in highly turbulent waters.



### Edible Oils: Toxicity and Other Impacts

Little or no information was found on aquatic toxicity of the compounds listed above. Since these oils are used for human food, they are not toxic to humans, and probably not likely to be directly toxic to aquatic organisms. Since they are relatively insoluble in water, they are not likely to be readily available to aquatic organisms. Any potential toxic effects would likely be short-term, since these oils do not accumulate in the food web. Several of the oils are listed as irritants to eyes for humans, so they could have the same impacts on marine mammals (USCG 1985).

Birds, however, may be impacted by edible oils, as reported by a paper on the impacts to birds of a spill of Canola oil. Impacts on the birds' thermoregulatory capabilities were disrupted, similar to the impacts that would be expected from petroleum oils. Feathers became matted and lost their waterproofing capabilities, eventually causing mortality to the bird (Smith 1989).

### Linseed and Tung Oils - Physical/Chemical Properties

Properties of linseed and tung oil are similar to those of the edible oils. Linseed oil is extremely viscous and polymerizes over time. Linseed oil is sometimes cut with organic solvents. A portion of the oil would form a residue and persist indefinitely. Tung oil is considered very insoluble, even in many organic solvents.

### Linseed and Tung Oils - Toxicity and Other Impacts

Effects listed for humans are irritation to skin and eyes. No specific information was found on aquatic toxicity. Smothering effects would be expected to be similar to edible oils.

### Tallow - Physical/Chemical Properties

Tallow (sheep and beef fat) is solid at temperatures below 40 degrees F (Merck 1989). If liquefied, smothering effects would be expected, as with edible oils.

### Turpentine, resins, rosin acids and tall oils - General

These oils are all closely related, since they are either components of each other or derived from pine sap. Toxicity information under resins are applicable to the other resin-related compounds.

### Turpentine - Physical/Chemical Properties

Turpentine is a liquid at room temperatures and dangerously flammable. The flash point is 95 degrees F with a lower explosive limit in air of 0.8%. It is lighter than water, has a relatively low solubility in water and is non-reactive.

### Turpentine - Toxicity

Turpentine oil was toxic to freshwater tadpoles (*Bufo bufo japonicus*) at concentrations of 5006 ppb (LC50 on a 72 hour static lab test; Nishiuchi and Yoshida 1974). Turpentine oil was also toxic to white shrimp (*Penaeus setiferus* - an estuarine species) from lab tests that injected undiluted product (Fontaine et al. 1975).

## Resin

### Resin acid, rosin acid - Physical/Chemical Properties

These are liquid at room temperatures and combustible. The flash point is 255-390 degrees F. It has a specific gravity equal to water, has a relatively low solubility in water and is non-reactive.

### Resin acid, rosin acid - Toxicity

Resin and rosin acids are toxic to Northern squawfish (a freshwater species - *Ptychocheilus oregonensis*) at 10 ppm (from a 24 hour lab test). Mortality occurred at this concentration in Chinook and Coho salmon fingerlings (MacPhee and Ruelle 1969). Resin acids can be bioconcentrated, but they also deplete quickly (Owens 1991). A bioconcentration factor of 200 was measured for rainbow trout (over 1 year old) over 96 hours at a concentration of 1.2ppm (Oikari et al. 1982).

### Rosin Oils - Physical/Chemical Properties

Similar to resin. Liquid at room temperature and combustible. The flash point is 255-390 degrees F. It has a specific gravity equal to water, has a relatively low solubility in water and is non-reactive. For toxicity, see Resin.

### Tall Oils - Physical/Chemical Properties

Tall oils are also referred to as liquid rosin and similar in properties. Liquid at room temperature and combustible. The flash point is 360 degrees F. It has a specific gravity lighter than water, has a relatively low solubility in water and is non-reactive. For toxicity see Resin.

### Alkaline Liquors from Pinewood digestion - Physical/Chemical Properties

The product found was specifically called Kraft Black Liquor and Kraft Pulping Liquor. It is solid (48%) and liquid (52%) at room temperatures. It is nonflammable, heavier than water, reactive (caustic) and will corrode aluminum, copper, and zinc metals. It is also normally transported cut with sulfuric acid (a regulated substance under CERCLA and SARA Title III) to make it less caustic. For toxicity see Resin.

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## BIRDS AFFECTED BY A CANOLA OIL SPILL IN VANCOUVER HARBOUR, FEBRUARY, 1989

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and

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### Introduction

Non-petroleum oil spills can affect waterbirds to a greater extent than spills of petroleum oils (McKelvey et al., 1980). Both oils affect aquatic birds by soiling the feathers and destroying their waterproofing qualities (Thorne, 1987; Hartung, 1967). Once this happens, water penetrates to the skin and the insulation and buoyancy afforded by the trapped air in the underlying down feathers is lost. In this condition birds suffer exposure and ultimately death, especially in winter and during harsh weather. Because vegetable oils are edible, they may not be considered as threatening to aquatic birds as petroleum oils when spilled. However, the end result is the same; birds die.

The purpose of this paper is to document the number of each aquatic bird species involved in a small spill of rapeseed oil (canola) which occurred in Vancouver Harbour on February 26, 1989.

### Spill Description

From approximately 2300 to 2340 h, February 26, 1989, a partially open bleeder valve on a dockside manifold, at Neptune terminals, allowed an estimated 1818L (400 gal) of rapeseed oil to spill into Vancouver Harbour during a product transfer operation. The spill site was located on the north shore of the harbour about 2 km west of the Second Narrows bridge (Figure 1). An aerial reconnaissance approximately 10 hours after the accident located the spilled oil and bird numbers in the inner harbour. At that time, a patchy slick of yellow oil stretched from the spill site to the centre of the harbour and a thin film of oil covered the entire harbour from Stanley Park to the Second Narrows bridge. No initial effort was made to contain the spill with booms and an attempt to disperse the oil with multiple passes of a small tug through the slick proved ineffective. At first light, Neptune contracted Sprayaway Marine Services to recover the spilled oil. Sprayaway deployed two self-propelled skimming vessels to recover oil and set up booms to contain oil for subsequent recovery.

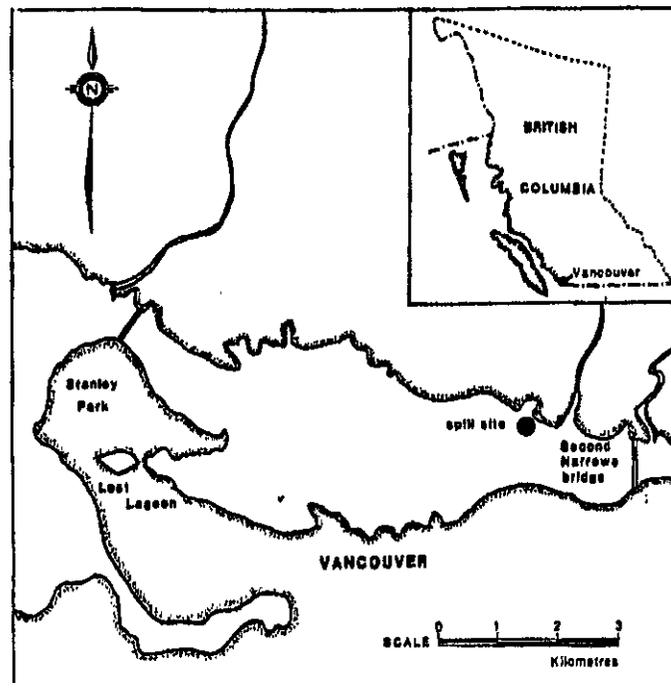


Figure 1 Vancouver Harbour, Showing the Site of the Rapeseed Oil Spill

### Cleanup Operations

Sprayaway concluded their cleanup operations at 1430 h on February 27th, some 15 hours after the spill was discovered. The skimmer boats pumped the effluent to tanker trucks which transported the oil/water mixture to a disposal site where it was mixed with sawdust and incinerated.

The Wildlife Rescue Association of B.C. (WRA), Society for the Prevention of Cruelty to Animals (SPCA), and Stanley Park Zoo were informed of the spill and began preparations to receive, clean, and rehabilitate oiled birds.

Birds submitted for cleaning and rehabilitation were treated primarily at the WRA facility in Burnaby. Cleaning procedures followed that of A. Berkner (1988, pers. com., oiled bird cleaning workshop). A continual supply of hot water, maintained at a specific temperature, is essential in an operation to clean oiled birds. A portable, propane-fueled, hot water heating system developed and described by McKelvey (1988) was loaned to the WRA, by the Canadian Wildlife Service, for this purpose.

### Impact

The aerial reconnaissance estimated that at least 700 birds were present in the harbour after the spill: 500

diving ducks (scoters, scaups, and goldeneyes), 100 gulls, and 100 other divers (grebes and cormorants). At 1600h, February 27th, about 2000 birds were counted around Stanley Park, of which 20 appeared to be oiled (J. Vanderhoven, pers. com.). On February 28th, over 300 oiled goldeneyes (mostly Barrow's *Bucephala islandica*) were seen crowded on islands in Lost Lagoon and remained there for two days (L. Lesage, pers. com.). Their numbers decreased over the next four days, presumably as birds cleaned themselves and returned to feeding areas around the harbour. A survey of the north shore of the harbour by boat, on March 1, 1989, revealed over 1040 birds of 12 species; only five individuals appeared to be oiled.

Oiled birds are usually not recovered until about three days after an oil spill. It generally takes that long for birds to become weakened to the point where they can be captured. The numbers of birds found in days subsequent to the spill are shown in Figure 2. The second peak which appeared on the seventh day after the spill, was largely composed of several Mallards which were secondarily oiled from an open reservoir on the spill site property which held some spilled oil. A total of 88 birds of 14 species were recovered from Vancouver waters after this spill (Table 1).

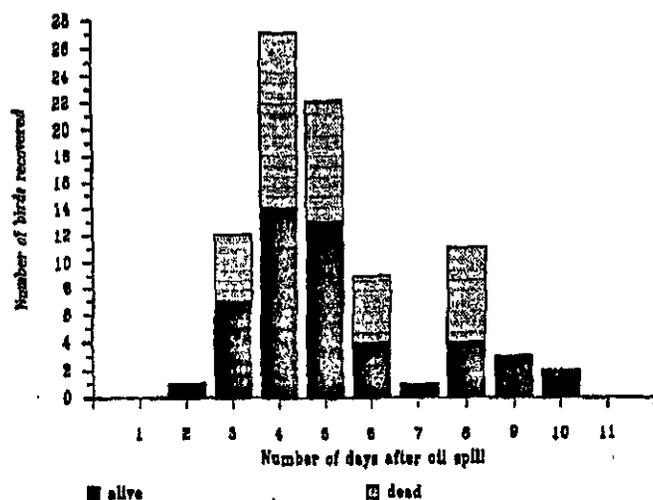


Figure 2 Numbers of Oiled Birds Found Each Day

## Discussion

When aquatic birds are oiled, their daily activity patterns are interrupted and more time is devoted to preening in an attempt to clean feathers. In winter birds normally spend a great portion of their time feeding (Paulus, 1988). Alteration of normal feeding patterns might affect survival, especially in winter when food resources are limited and energy requirements are high. Reduced feeding may increase recovery time or weaken the bird to the point of no return. In the state of thermoregulatory stress that an oiled bird experiences, energy requirements

are higher than normal just to maintain body heat (Hartung, 1967). Distraction from feeding for increased preening will accelerate metabolic draw on stored resources and weaken birds further. In this weakened state, birds also become more susceptible to disease.

Even if a bird survives the initial oiling, the long-term effect of ingested oil and physiological stress may severely inhibit its longevity and reproductive ability. Ingestion of petroleum oil has been shown to inhibit fecundity in birds prior to egg laying (Ainley et al., 1981; Fry et al., 1986). Hartung (1966) tested the toxicity of a variety of industrial oils ingested by waterfowl and found the effects were: lipid pneumonia, gastrointestinal irritation, fatty changes of the liver, and adrenal cortical hyperplasia. The physical effects of the ingestion of vegetable oils is not known; however, subsequent deaths of recovering oiled birds was unexpected. Some other factor related to ingestion of vegetable oil may have been responsible.

Over 144 000 tonnes of grain oils were shipped through Vancouver Harbour in 1988 (Vancouver Port Corp.). The spill of 1818L (400 gal) on February 26th accounted for a negligible portion of the volume handled. Nevertheless, effects of such a small spill could be observed on aquatic birds. This may be of particular concern to Barrow's Goldeneye as more than 80% of the world population breeds in B.C. (Savard, 1988) and Vancouver Harbour is one of the more important wintering sites within the Strait of Georgia (Savard, 1989). Almost 24% of birds recovered from this spill were Barrow's Goldeneye.

The bulk of spilled oil was in the harbour for about 15 hours, which resulted in at least 88 aquatic birds being oiled. Many of these birds were found dead and over half of the birds found alive subsequently died during treatment. The number of casualties is likely higher than recorded for various reasons. Predator pressure is high in winter and dead and dying birds would quickly be taken by raptors and scavengers. Long-term effects of ingested oil, manifested later, makes it difficult to relate to this spill. Heavily oiled birds may sink once oiled and would not be recorded.

Rehabilitation is one way to mitigate the effects of oil spills on aquatic birds. However, the percentage of birds that can be released is small and their chance of survival is unknown.

Containing and recovering oil as soon as possible after it is spilled is the best alternative. Ships transferring any such product should be surrounded by booms that would prevent any spilled oil from escaping into the harbour. Transfer lines should be tested before use to check for leaks. The system should be monitored during transfers and spill detection equipment should be in place to alert the operators to any problem. On-site personnel should be trained and prepared to initiate an emergency/contingency plan in the event of a spill. This would include the immediate reporting of any spill to Environment Canada,

Table 1 Species Composition of Aquatic Birds Recovered

species	Number of Bird Recovered			
	Dead	Alive	Released'	Totals
1. Western Grebe	2	3	1	5
2. Red-necked Grebe	0	3	2	3
3. Horned Grebe	4	8	7	12
4. Pelagic Cormorant	1	1	0	2
5. Malfard	5	12	7	17
6. American Wigeon	5	0	0	5
7. Ring-necked Duck	2	0	0	2
8. Greater Scaup	0	2	0	2
9. Lesser Scaup	2	0	0	2
10. Surf Scoter	0	1	0	1
11. Barrow's Goldeneye	8	13	4	23
12. Common Goldeneye	7	4	1	11
13. Bufflehead	1	1	1	2
14. Red-breasted Merganser	0	1	0	1
15. Unidentified	2	0	0	2
Totals	39	49	23	88

'birds released after rehabilitation

the Coast Guard, and the Harbour Commission. Edible, non-toxic vegetable oils pose environmental hazards which may not be considered as dangerous as petroleum oil products. These hazards must nevertheless be emphasized.

### Acknowledgements

We thank Paul Ross of Environment Canada, for his role in coordination and communication among all groups involved. We also thank the Vancouver Police Department for providing the crew and boat VPD-99 to conduct the survey of Vancouver Harbour. We thank W.S. Boyd, A. Breault, R. Butler, R. McKelvey, and J-P.L. Savard for reviewing previous drafts of this paper and for their numerous suggestions for improvement.

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## CANOLA OIL AS A SUBSTITUTE FOR CRUDE OIL IN COLD WATER SPILL TESTS

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### INTRODUCTION

The physical properties and behavioral characteristics of Canola oil (also known as rape seed oil) were assessed and compared with Prudhoe Bay crude oil under a variety of conditions in the cold chambers at the University of Alaska, Anchorage. Emphasis was placed on the feasibility of using this nontoxic vegetable oil for testing containment and recovery equipment in cold climates, focusing on its potential applications involving oleophilic/sorbent recovery systems with or without ice.

Several physical properties of Canola oil and Prudhoe Bay crude oil were determined at controlled temperatures. Specific gravities were measured over temperatures ranging from  $-23^{\circ}\text{C}$  to  $27^{\circ}\text{C}$  using standard petroleum hydrometers and were found to vary in a linear fashion (Figure 1). The specific gravity of the Canola oil was approximately 4% higher than that of the crude oil over the indicated temperature range.

The viscosities of the oils were measured at temperatures from  $-18^{\circ}\text{C}$  to  $27^{\circ}\text{C}$ . Figure 2 contains plots of the measured viscosities for Canola oil, Prudhoe Bay crude oil and Norman Wells crude oil. The Prudhoe Bay and Norman Wells crude oil viscosity data represented by dashed lines were obtained from Figure 3-18 of the ABSORB Oilspill Contingency Plan (1980). The Canola and Prudhoe Bay crude oil viscosity data shown as solid lines are those determined in this experiment. The pour point of the Canola oil was also examined and was estimated to be  $-26^{\circ}\text{C}$ . That of the Prudhoe Bay crude oil, approximately 10% evaporated, is  $-25^{\circ}\text{C}$  (ABSORB, 1980).

The interfacial tension between the Canola oil and distilled water at  $25^{\circ}\text{C}$  was found to be 11.1 dynes/cm, while the interfacial tension between Prudhoe Bay crude oil and distilled water was measured as 26.8 dynes/cm. In tests on evaporation rates, there was no measurable weight loss for the Canola oil during the test period. The results for the crude oil are shown in Figure 3.

The behaviour of Canola oil and crude oil in the presence of rope mop fibres, sorbent pads, and ice was examined. All tests were conducted with prepared seawater mixtures (approximately 35 parts per thousand), polypropylene fibres removed from a section of ABSORB's ARCAT\* skimming system, small squares of nonwoven polypropylene microfibre, and ice prepared from the same seawater mixtures. The objectives were to assess the oleophilic properties of each of these media while noting the rates of oil uptake and release. A simple oil-and-water shake test was also conducted under warm and cold conditions, to compare the tendencies for Canola oil and crude oil to emulsify with seawater.

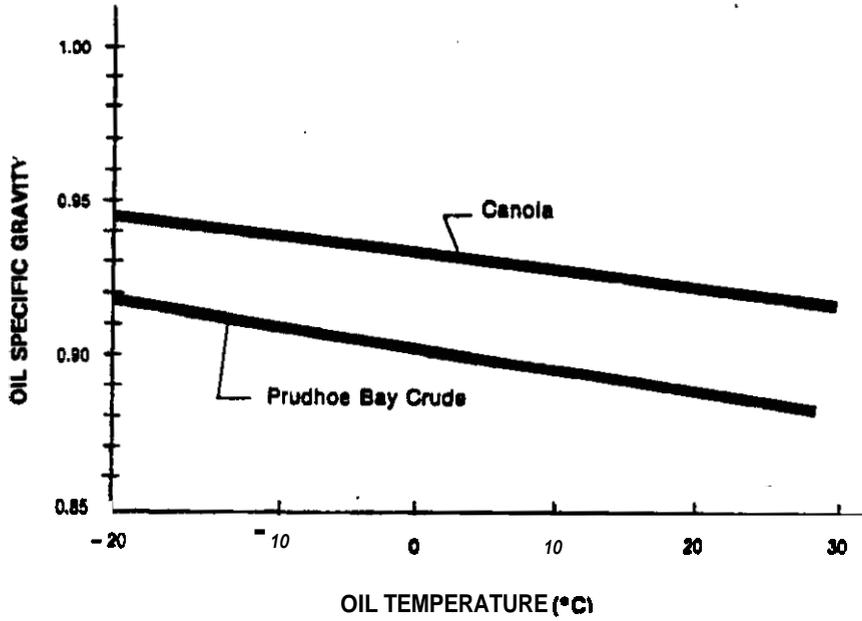
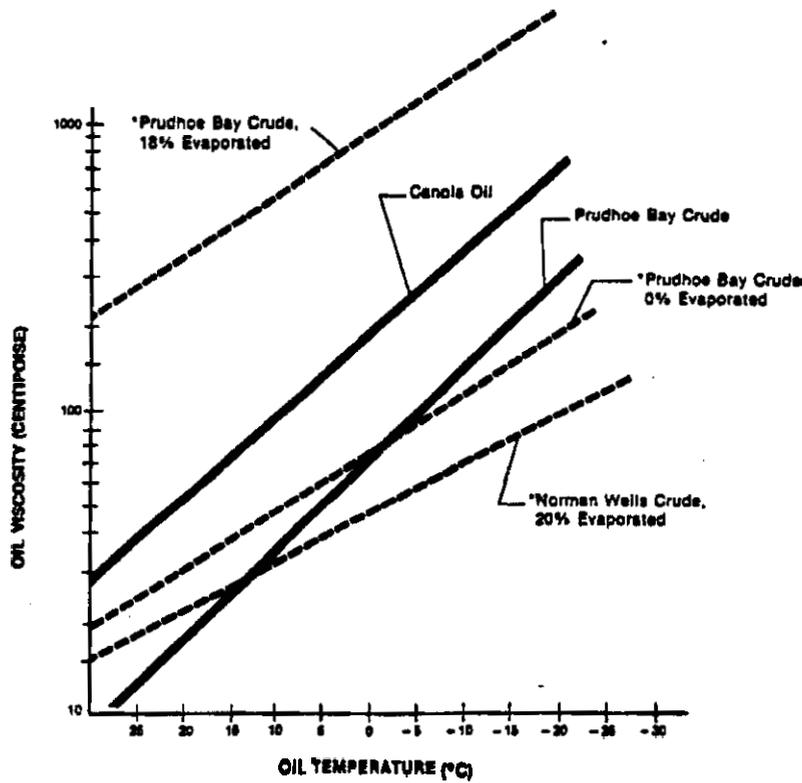


FIGURE 1 SPECIFIC GRAVITY OF CANOLA AND PRUDHOE BAY CRUDE OIL VERSUS TEMPERATURE



\*ABSORB OIL SPILL CONTINGENCY PLAN, Figure 3-18.

FIGURE 2 CANOLA VISCOSITY VERSUS CRUDE OIL VISCOSITY

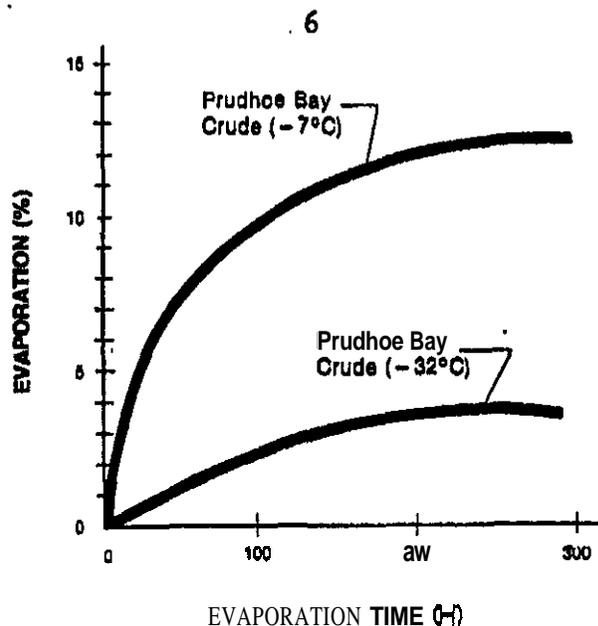


FIGURE 3 MEASURED EVAPORATION OF PRUDHOE BAY CRUDE OIL VERSUS TIME AND TEMPERATURE (Air Speed Variable at  $\approx 2$  m/s)

In tests to determine oil adhesion, the rope mop fibres were observed to reach an apparent saturation level within a few seconds. The volumes of oil plus water recovered for crude oil ranged from 1.5 to more than 8 g per dip. Figure 4 illustrates these comparative recovery rates for the two oils showing how the recovered volume in each case increased with decreasing water and air temperatures.

The recovered volume of Canola oil in warm air tests was twice that of crude oil, but only 40-50% greater in cold air tests. These latter tests are more representative of the actual operating conditions a rope mop skimmer might be subjected to during winter and breakup recovery operations on a cleared (ice-free) pool of oil and water. Should such a field test be conducted using Canola oil, these laboratory (cold-room) experiments suggest that the recovered volumes (for a saturated rope mop) would very likely be 40 to 50% greater than the actual volumes had fresh Prudhoe Bay crude oil been used.

The oil-to-water ratios for the recovered volumes was bound to vary between the two oils, as shown in the boxes of Figure 4. The rope mop fibres picked up between 19 and 23% water when used with Canola oil, while the water uptake with crude oil varied between 8 and 10%. Allowing for the lower water contents found in the crude oil test, these tests suggest that a field test with Canola oil and rope mop fibres would likely involve oil recovery rates that are 30 to 40% greater than the actual oil recovery rates had fresh Prudhoe Bay crude oil been used. These comparisons, of course, depend upon a sufficient thickness of oil being available to saturate the rope mop fibres.

Tests involving warm water/warm air and cold water/cold air were also undertaken to evaluate the comparative uptakes of Canola oil and crude oil in sorbent pads. The volumes of oil absorbed by the pads in each of the two tests are shown in Figure 5. The dashed lines are provided only to suggest a possible trend in the oil uptake data for the

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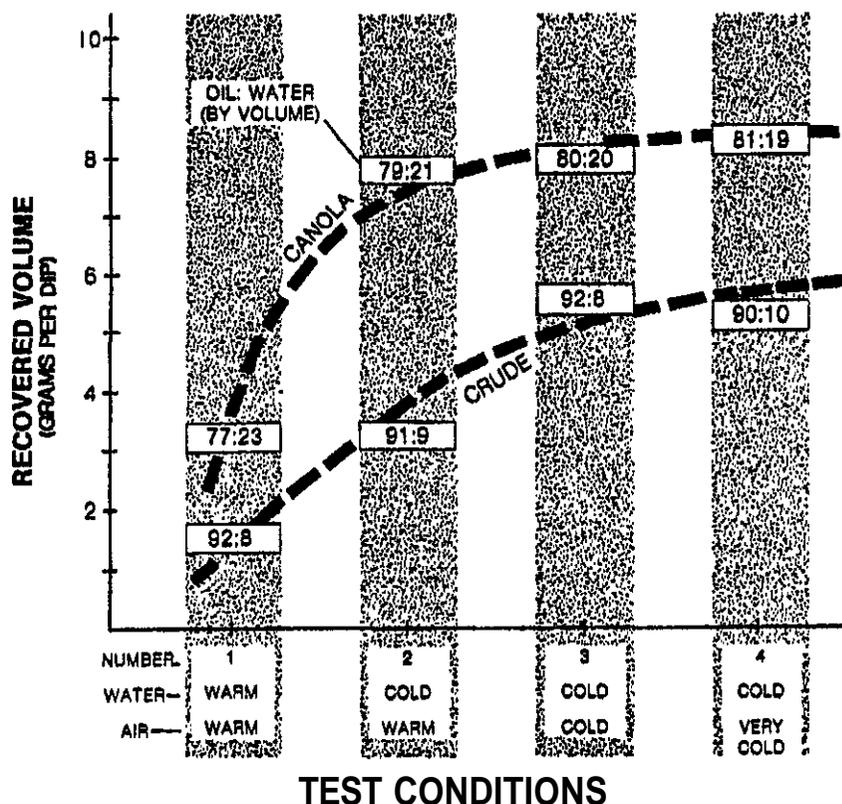


FIGURE 4 ROPE MOP RECOVERY WITH CANOLA AND CRUDE OIL

air/water test conditions being examined. During the 15 second exposure tests, only the warm crude oil in Condition 1 was found to penetrate and saturate each pad (requiring 3 seconds). Whether warm or cold, however, crude oil absorption per pad remained about 1 grain higher than with the Canola. The drop in recovered oil at the colder temperatures is consistent with the expected reductions in penetration with increased viscosities.

When the pads were permitted to saturate, however, the absorbed volumes were nearly the same for crude oil and Canola oil, the amounts ~~increased~~ with the reduced temperatures. Once saturated at the colder temperatures (requiring about 2 minutes), there was a tendency for more oil to adhere to the outer surfaces of the sorbent.

Ice adhesion tests were conducted with air and water temperatures at or slightly below 0°C. During each test, the cubes of ice were exposed to the oil for 2 minutes. A wire screen was then used to lift the oiled ice above the surface, where it was allowed to drain for 1 minute. The thickness of the oil layer and the condition of the oiled ice were then noted, and a clean batch of ice was placed in the oil. In separate tests, cubes of sea ice were pushed down through the oiled surface, and the degree of oil adhesion to the ice was noted.

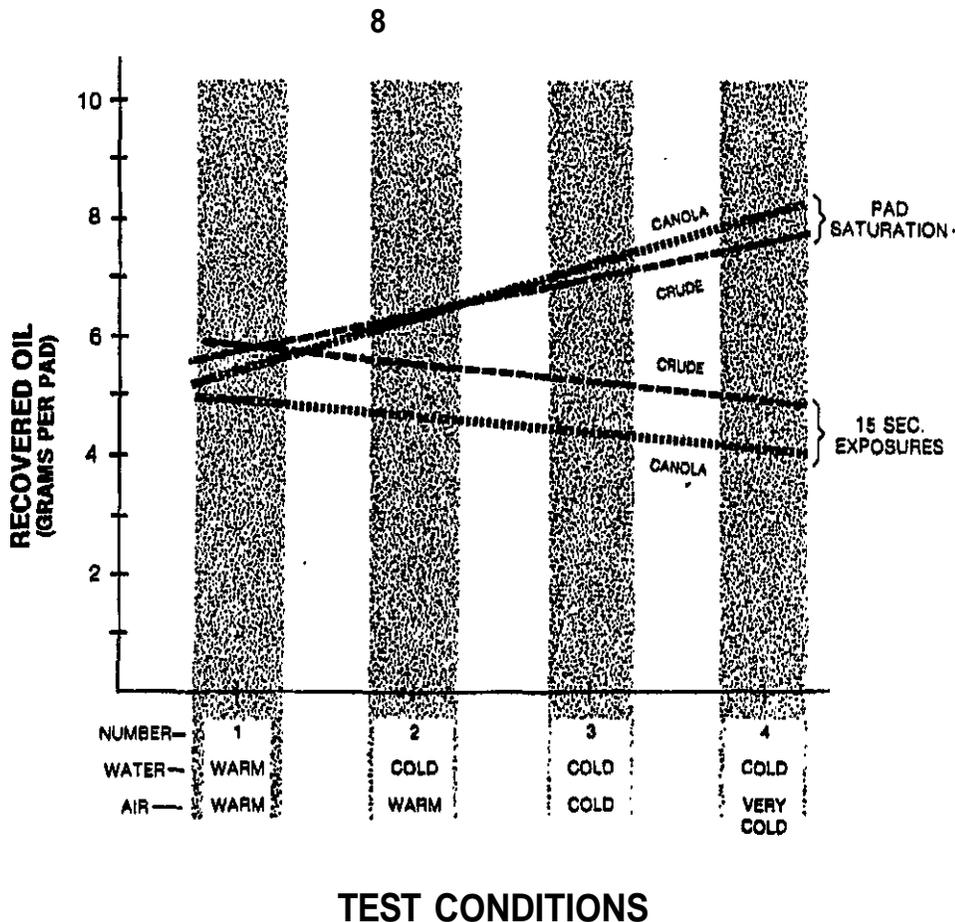


FIGURE 5 SORBENT PAD RECOVERY WITH CANOLA AND CRUDE OIL

Both the Canola oil and the crude oil had the same tendency to coat the sea ice as it was placed through the oil/water interface of each container. The oil would not stick to any portion of the ice surfaces that remained below the oil/water interface; however, the upper surfaces became coated with both oils and remained coated even after removal from the container. The volumes of oil removed during each ice lift were identical for both oils. Because of the reduced air temperatures, the oil in each case remained on the ice, with very minor release until disposed of the following day.

It was noted that neither the Canola nor the crude oil would stick to the sea ice when the ice was pushed completely beneath the oil/water interface. The Canola had a slightly greater tendency to stay on a horizontal underside; however, the slightest agitation of the ice would free it from any remaining oil. This lack of oil adherence to submerged sea ice even after surface coating is of significance in the development of improved oil recovery equipment for use in broken ice.

The comparison of tendencies for Canola and Prudhoe Bay oils to become emulsified by agitation was examined under warm (24°C) and cold (0°C) conditions. The shake test under warm conditions produced water-in-oil emulsions quite unlike those produced during

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the cold (0°C) test, The results of each test are illustrated in Figure 6. In the warm test with Canola oil, a small water-in-oil emulsion formed immediately after shaking. Canola oil and water gradually separated out of the mixture. In contrast to this stable emulsion, the warm crude oil took up seawater immediately after shaking (i.e., 95% of the content was water-in-oil emulsion), and about 1.5 hours were required for the clear-water volume to return to 40 mL. The nature and extent of water droplet entrainment within the oil could not be assessed visually because of the crude oil's opacity.

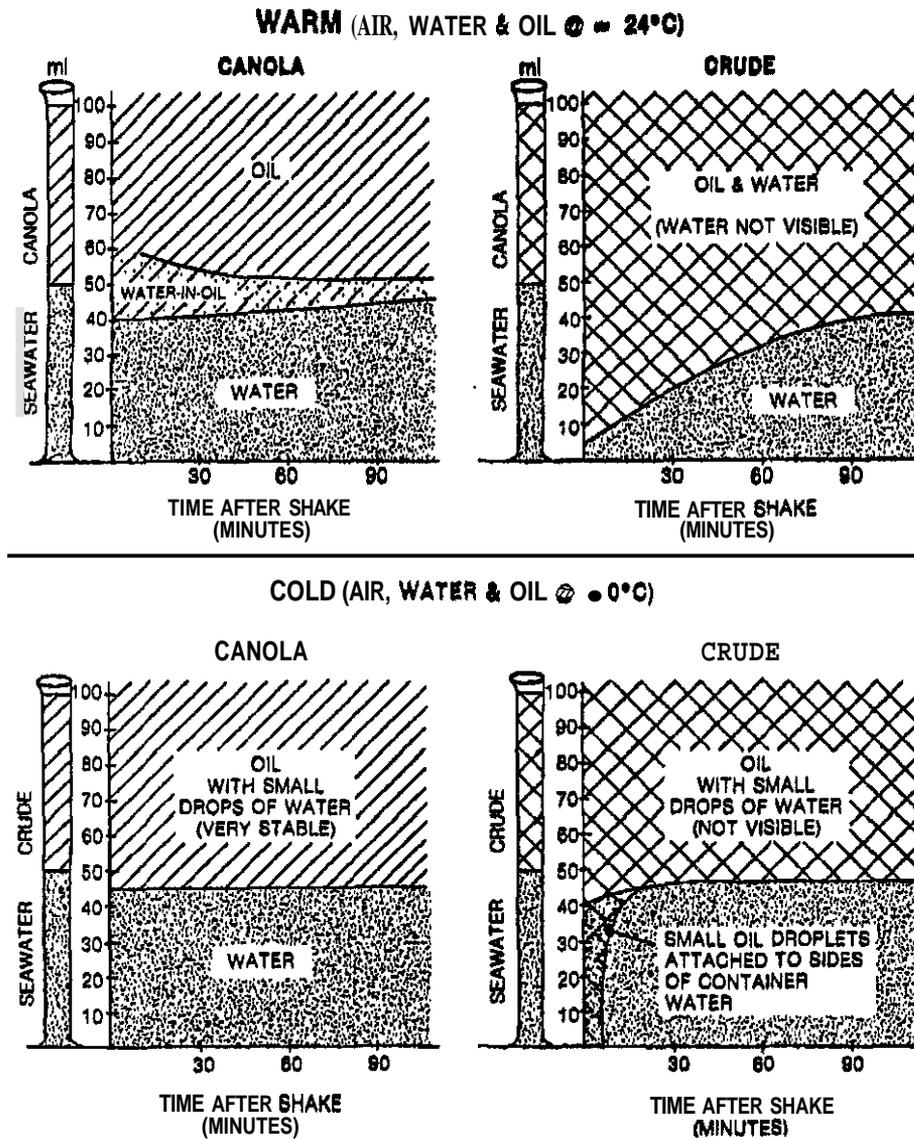


FIGURE 6 EMULSIFICATION TESTS - CANOLA AND CRUDE OIL

During the cold test, both oils revealed a tendency to avoid emulsification. Some of the crude oil broke into small globules within the water column; however, the majority of these globules quickly rose and recombined with the overlying oil layer. Only a few small,

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globules remained for the first 20 minutes attached to the walls of the cylinder in the water column. Shortly after both cylinders were shaken, it was clear that very little water had been entrained in each of the oils. The Canola oil and the crude oil took on approximately 10% of the original water volume as a stable portion of the overlying oil.

The results of these cold-chamber tests suggest that Canola oil can be used as a viable substitute for crude oil during the field testing of certain types of spill control equipment, with or without the presence of broken ice. Observations made during the laboratory tests can be summarized as follows:

- (a) The specific gravity and the viscosity of Canola oil vary linearly with temperature. The variation of its viscosity with temperature suggests that Canola oil represents a "medium weight" oil that is comparable to a lightly weathered Prudhoe Bay crude oil (i.e., about 10% evaporated).
- (b) The volume of Canola oil used during a spill test will remain unaffected by the usual influence of evaporation.
- (c) Canola oil exhibits an affinity for oleophilic surfaces which is quite similar to that of crude oil. Canola oil's greater viscosity (compared to fresh Prudhoe Bay crude oil) results in a 30 to 40% increase in oil recovery rate with saturated rope mop fibres under Arctic air and water temperatures.
- (d) Canola oil penetrates the fibres of sorbent pads at a slightly slower rate than does fresh Prudhoe Bay crude oil; however, saturation of the pads can be accomplished within minutes and the recovered volumes of Canola and crude oil are nearly identical.
- (e) Canola oil and Prudhoe Bay crude oil have the same tendency to coat the surface of sea ice drawn up through an oil/water interface. Both oils also showed the same tendency to slide off submerged ice surfaces quite rapidly and completely.
- (f) Under cold air, water and oil temperatures (0°C), both the Canola and the crude exhibited similar tendencies for emulsification. Each oil took on approximately 10% of its original volume in water globules which did not settle out for several hours following the original 1 minute shake test.

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# PROPERTIES AND EFFECTS OF NONPETROLEUM OILS

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## ABSTRACT

Legislative history of water pollution control has not included detailed scientific definitions of what is meant by the rather inclusive term "oil." Because of the publicity surrounding spills of crude or petroleum-derived oils, little attention has been focused on non-petroleum oils. Approximately 5% of the oil spills reported to the Environmental Protection Agency are nonpetroleum oils. Their physical and chemical properties and adverse environmental effects are strikingly similar to the behavior of petroleum oil in the aquatic environment. This paper presents a comparative analysis of the properties and effects of petroleum versus nonpetroleum oils. Their similarities prove that these oils should be treated as one entity regardless of their origin. Finally, additional guidelines are presented to provide a wide broadly applicable distinction between oil and other hazardous materials for enforcement purposes.

## INTRODUCTION

Section 311 of the Federal Water Pollution Control Act amendments defines oil as "oil of any kind or in any form including, but not limited to petroleum, fuel oil, sludge, oil refuse, and oil mixed with wastes other than dredged spoil." Unfortunately, legislative history of water pollution control has not included detailed scientific definitions of what is meant by the rather broad term "oil." The Environmental Protection Agency has interpreted the definition of oil to apply to nonpetroleum as well as petroleum oil.

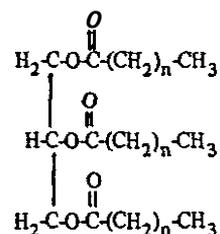
Petroleum oils are mineral or hydrocarbon oils produced from crude petroleum, while nonpetroleum oils consist of fatty oils derived from vegetable or animal fats and essential oils derived from plants. Because the fatty oils are produced in larger quantities and have a higher spill incidence than essential oils, this paper focuses on the harmful effects of discharges of vegetable oils and animal fats. Approximately 5% of the oil spills officially reported to the Environmental Protection Agency by a variety of producing and handling companies are nonpetroleum oils. Their physical and chemical properties and adverse environmental effects are strikingly similar to those of petroleum oils.

The objective of this paper is to compare the effects of petroleum and nonpetroleum oils in the aquatic environment. Case histories are described to underscore the similarities, and guidelines are presented for distinguishing all kinds of oil from other hazardous materials where the previous rationale fails to provide a clear distinction.

### Physical and chemical properties

Vegetable oils and animal fats are water-insoluble substances which consist predominantly of glyceryl esters of fatty acids, or triglycerides [1]. Triglycerides contain approximately 95% fatty

acids and 5% glycerol combined as Hers, with the following general structure:



They serve as an important source of free fatty acids which are released by caustic hydrolysis of the ester bonds. Because the fatty acid radicals constitute the greater part of the glyceride molecule, the chemical and physical properties of vegetable oils and animal fats are determined largely by the properties of its component fatty acids.

Fatty acids are defined as carboxylic acids derived from or contained in animal fats or vegetable oils. All fatty acids are composed of a saturated or unsaturated hydrocarbon chain of alkyl groups containing from 4 to 22 carbon atoms and characterized by a terminal carboxyl group [2]. Fatty acids in vegetable oils are mostly 16 and 18 carbons in length, while in animal fats 20 and 22 carbon chains are found as well.

Petroleum and most high-volume petroleum products are extremely complex mixtures of chemical compounds. Many classes of compounds are present in petroleum, and each class is represented by many components. For example, hydrocarbons are a major class of constituents of petroleum. The hydrocarbons include the subclasses normal, branched, cyclic, saturated, and aromatic hydrocarbons. The subclass of normal hydrocarbons is represented by 10 to 60 individual members in many petroleum oils and products [3].

Similar behavior of fatty acids and petroleum oil in the aquatic environment is largely a result of their predominantly hydrocarbon character. Because of common physical and chemical properties, a parallel can be drawn between animal fats and oils, vegetable oils, fatty acids, and petroleum oils. Properties attributed to the long-chain hydrocarbons present in all fats and oils are summarized below:

1. limited water solubility and high solubility in organic solvent,
2. formation of surface slicks, and
3. ability to form emulsions and sludges.

Because animal fats and vegetable oils share similar physical and chemical properties with petroleum oil, the Environmental Protection Agency considers them a potential danger to the aquatic environment.

Other evidence supporting the similarity of nonpetroleum oils to petroleum oils is the use of the same analytical method to detect

and measure both substances. For purposes of water pollution control, this lends additional credence to the interpretation that these substances should be regulated in a similar manner. The oil-and-grease method approved by the Environmental Protection Agency in Guidelines Establishing Test Procedures for Analysis of Pollutants is the procedure described in *Standard Methods for the Examination of Water and Wastewater* [15]. If employed, liquid-liquid extraction with trichlorotrifluoroethane as the extracting solvent. The method has found acceptance as the analytical parameter in water quality assessment such as the National Pollutant Discharge Elimination System (NPDES) permit program and effluent guideline limitations. The oil-and-grease procedure is the only method approved as standard, and it does not distinguish between petroleum and nonpetroleum oils.

Although standard analytical methods could be developed to differentiate between petroleum and animal or vegetable derived materials, no such development has been required to address the relevant water pollution aspects of the two contaminants. The physical and chemical properties and environmental effects of both types of materials are sufficiently similar to negate the need for differentiation.

Associated with the low solubility and density of nonpetroleum oils is their ability to form a layer on the surface of the water. This occurs because of the presence of the hydrophilic ester bonds, which dissolve in water, and the hydrophobic hydrocarbon chain which is water insoluble and therefore distributes itself on top of the water. This monomolecular layer covering the surface of the water produces a sheen. Although due to a different phenomenon, this property is common to petroleum oils as well and is used by the Environmental Protection Agency as a test to determine whether oil has been spilled in sufficient quantity to be harmful.

### Environmental effects

The effects of nonpetroleum oils are similar to the effects of petroleum oils because of the physical properties common to both. Like petroleum oils, vegetable oils, animal fats, and mixed fatty acids may occur at four levels of the aquatic environment: (1) floating on the surface, (2) emulsified in the water column, (3) solubilized, and (4) settled on the bottom as a sludge. Associated with the ability to form surface films and slicks is the ability to form emulsions under proper environmental conditions. Conditions such as agitation by surf action, wind current, rapidly flowing streams, and prolonged exposure to heat from sunlight may lead to the formation of emulsions at the water-solid interface. When the emulsions and surface films or masses become engaged with debris, they can settle to the bottom as a sludge.

Oily substances of any kind may possibly be harmful to aquatic life and waterfowl in the following manner:

1. Free oil and emulsions may act on the epithelial surfaces of fish. If the concentration of oil is too heavy, oil will accumulate on the gills and prevent respiration. Oil and emulsions may mat and destroy algae and other plankton, thereby removing a source of fish food. The coated organisms may agglomerate with suspended solids and settle to the bottom.
2. Settled oily substances may coat the bottom, destroy benthic organisms, and interfere with spawning areas.
3. Soluble and emulsified material, ingested by fish, taint the flavor and may cause intestinal lesions due to laxative properties.
4. The biochemical oxygen demand (BOD) of organic materials may deoxygenate the waters sufficiently to kill fish. Heavy coatings of free oil on the surface may interfere with the natural processes of reoxygenation and photosynthesis.
5. Water-soluble constituents may exert a direct toxic action on fish or fish-food organisms [6].
6. Lethal effects on waterfowl may be drowning because of loss of buoyancy, exposure because of loss of insulating capacity of feathers, and starvation and vulnerability to predators due to lack of mobility [7].
7. Adverse aesthetic effects are fouling of shorelines and beaches. There and other effects have been observed and are documented for petroleum and vegetable oil spills. Case his-

ories discussed in the following section will illustrate some of the harmful effects outlined above.

Some vegetable oils and inedible tallow and greases are characteristically high in free fatty acids (3-30%) [2]. The fatty acids are considered as weak acids because of the limited degree to which they ionize. Their toxicity is dependent on the soluble salt form. Solubility calculations indicate that fatty acids are sufficiently soluble to exceed the toxicity threshold for fish [6,8]. Such salts can be formed in natural waters, but the extent of their formation is dependent on the chemical character of the receiving water. The short-chain and aromatic components of petroleum oil are analogous to the soluble and toxic fatty-acid salts.

In the aquatic environment, a surface film or shore accumulation of unsaturated oils or mixed fatty acids can undergo oxidation-polymerization reactions by contact with air [1]. The process has very similar effects to those observed in the "weathering" of petroleum oils. Although the weathering mechanisms of the two materials are not the same, the hardening of exposed surfaces and the formation of heavy sludges are common to both. The primary processes affecting petroleum oil in the aquatic environment are evaporation of the more volatile constituents, dissolution of the more soluble components and preferential oxidation by microorganisms [3].

### Case histories

Oil spills affecting the Minnesota and Mississippi rivers. The largest and most important occurrence to date of a spill of vegetable oil has been the discharge of approximately 2-1/2 million gallons of crude soya and salad oil into the Minnesota and Mississippi Rivers in the winter of 1962-1963 [9]. This spill provided an opportunity for detailed examination of the effects of vegetable oil on the aquatic biota, birds, and mammals. It was spilled into the Blue Edith River, 1/4 mile above the Minnesota River. Because it was winter, the oil moved over and under the ice and congealed or was trapped until the spring.

At the end of March and in early April, the ice thawed and significant amounts of soybean and salad oil went down the Minnesota River to the Mississippi and into its backwaters and lakes. Evidence of oil was found as far as 250 miles downstream from the initial spill site. Dead waterfowl were observed along approximately 60 miles of the Mississippi River, concentrating in lake and backwater areas where the oil became lodged in marshes and on shorelines.

The Minnesota Department of Conservation estimated at least 4,000 and probably more birds died, while another 1,300 were rescued. The causes of death were determined to be several:

1. drowning because of loss of buoyancy when feathers became coated
2. exposure because of loss of insulating capacity of feathers when penetrated by oil
3. starvation and vulnerability to predators caused by loss of mobility in air and water
4. intestinal lesions caused by laxative properties of oil
5. suffocation as a result of nostrils and throat becoming clogged.

All of these effects have also been reported as causes of death for waterfowl destroyed by spills of crude petroleum oil.

Standard 5-day and long-term BOD tests indicated that the crude soya oil had an ultimate BOD of several hundred thousand milligrams per liter. This value, however, applies only to the original oil when it is uniformly dispersed in solution. Under environmental conditions of the spill described above, oils clumped and formed rubbery floating masses instead of dispersing. When oils fail to disperse, large surface areas are not exposed to bacterial action, and the oxygen demand created by the oil does not have a significant effect on the dissolved oxygen concentration unless the dissolved oxygen is already depressed to a dangerously low level by other pollutants. A more serious effect could result in smaller water bodies or when more complete mixing occurs. The floating and settled oil masses or clumps taken from the river or picked up on shore exhibited a relatively slow degradation.



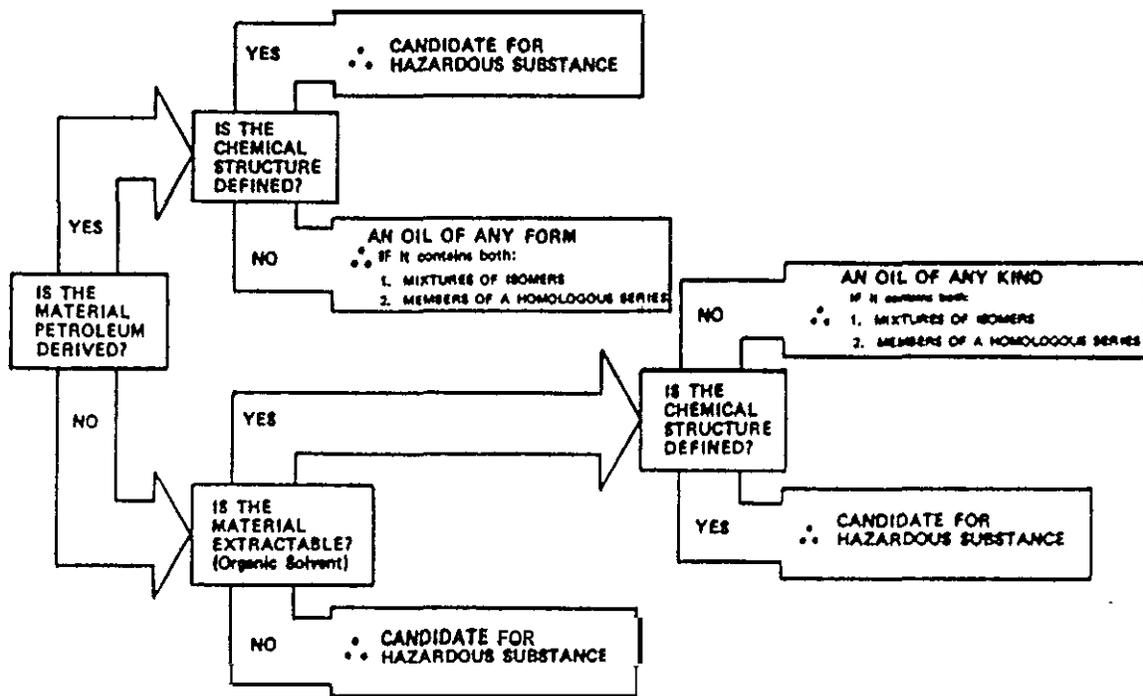


Figure 1. Rationale for distinguishing between oils and materials that may be hazardous substances

hydrocarbons. Materials of category 1 are members of an homologous series in which each successive member has one more  $\text{CH}_2$  group in its molecule than the next preceding member. Fats are composed of fatty acids, which are long-chain aliphatic acids, both saturated and unsaturated. Members of category 2 differ by two  $\text{CH}_2$  groups. Compounds of category 3 contain multiples of five carbon atoms so related to each other as to allow dissection of their structures into isoprene-like fragments. Oils of all three categories contain multiples of isomers.

For example, kerosene contains as a major constituent straight and branched aliphatic hydrocarbon isomers with carbon numbers mostly in the range of  $\text{C}_{11}$  to  $\text{C}_{16}$ . They form three or more members of an homologous series differing by a  $\text{CH}_2$  group, and therefore, kerosene is as an oil. Vegetable oil is an edible oil generally composed of mixtures of triglycerides. Because vegetable oils contain isomers of triglycerides composed of three or more saturated and unsaturated straight-chain fatty acids differing by two  $\text{CH}_2$  groups in length, they qualify as an oil.

Under these new criteria, PCBs and toxaphene do not qualify as oils, because the members of the homologous series do not differ by a carbon-containing increment. PCBs and toxaphene are composed of a multitude of isomers, and the homologous series increment, instead of containing carbon, is made up of a Cl atom. A mixture of benzene, toluene and isomers of xylene qualify as oil under the conditions of the test.

In summary, the guidelines presented here are not intended to replace the rationale published in the 1911 Thompson paper, but rather serve as an adjunct to the previous criteria. Since the publication of the proposed hazardous substances list, this document provides additional guidance in the decision-making process of characterizing borderline materials. In complex cases where the distinction between oil and hazardous materials is not clear, it may still be necessary to have decisions based on such additional considerations as percent composition of mixture, relative degrees of toxicity, and ease of removal.

## CONCLUSION

Based on the data presented in this report, parallels can be drawn between animal fats and oils, vegetable oils, fatty acids, and petroleum oils. Because of their common physical and chemical properties, the adverse environmental effects of nonpetroleum oils are strikingly similar to those of petroleum oils. The cited case histories illustrate that the behavior of nonpetroleum oil in the aquatic envi-

ronment is analogous in many respects to the behavior of petroleum oil. Although not specifically mentioned, methods and procedures for the removal of both types of oil from surface waters are also similar. The guidelines for distinguishing between oil and other hazardous materials provide a more broadly applicable distinction for enforcement purposes. *M* evidence clearly supports the Environmental Protection Agency's position that nonpetroleum oils are subject to the oil regulations under section 311 of the FWPCA.

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